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Title of manuscript: Manufacture and characterisation of porous ferroelectrics for piezoelectric energy harvesting applications

Authors: J. I. Roscow¹, J. Taylor² and C. R. Bowen¹

Address: ¹Materials and Structures Centre, Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, UK

²Department of Electrical and Electronic Engineering, University of Bath, Bath, BA2 7AY

Contact email address: j.i.roscow@bath.ac.uk

Abstract

Porous ferroelectric materials have been evaluated for their piezoelectric energy harvesting capabilities. Macro-porous barium titanate (BaTiO₃) ceramics were fabricated with a range of porosities using the burned out polymer spheres process. The pore fraction was tailored by mixing a pore forming agent with BaTiO₃ powder in varying amounts by weight before cold-pressing and pressureless sintering. Introducing porosity into the ferroelectric significantly increased the energy harvesting figure of merit; with a maximum of 2.85pm²/N obtained at ~40% relative density compared with ~1.0pm²/N for the dense material. The results demonstrate that introducing porosity into a piezoelectric provides an effective route to improving the vibration energy harvesting capability of these materials.

Introduction

Interest in energy harvesting devices has grown in recent years with a view that they can replace or prolong the lifespan of batteries used to power a range of low-power electronic devices, such as wireless sensor arrays [1]. Ferroelectric materials, such as lead zirconate titanate (PZT) and barium titanate (BaTiO₃), are of particular interest due to their effective piezoelectric and pyroelectric properties, which enable them to harvest energy from both mechanical vibrations and temperature fluctuations.

Porous ferroelectric ceramics, particularly PZT, have been extensively studied, but effort has focussed predominately on the development of porous piezoelectrics for hydrostatic sensor applications, such as active and passive SONAR [2]. This is due to superior hydrostatic piezoelectric

strain and voltage coefficients, d_h and g_h , respectively, found in porous materials compared to dense materials. A reduction in relative density due to the introduction of porosity also reduces the acoustic impedance of transducers used in water or on biological tissue, thereby increasing the efficiency of energy transfer from one medium to another. These applications have dominated research into porous ferroelectrics to date, with little interest shown into the benefits for energy harvesting.

Energy harvesting FOMs have been derived for low frequency, off-resonance mechanical excitation of polycrystalline piezoelectric ceramics [3], conditions that mean the material can be assumed to behave as a parallel plate capacitor. The energy stored, u , in a material as a result of an applied stress is therefore equal to:

$$u = \frac{1}{2} d_{ij} \cdot g_{ij} \cdot T^2 \quad (1)$$

where d is the piezoelectric strain coefficient, g is the piezoelectric voltage coefficient, T is applied stress and subscripts i and j denote the direction of application and response, respectively. Eqn. 1 is derived from the energy stored in a capacitor ($U = \frac{1}{2}CV^2$) (where C is capacitance and V is applied voltage). If the force is applied along the poling axis, which convention defines as the 3-direction, the materials related FOM is [3]:

$$FOM_{33} = d_{33}^2 / \epsilon_{33}^T \quad (2)$$

where ϵ_{33}^T is the relative permittivity at constant stress. Previous studies have shown that only a small reduction in d_{33} occurs when the relative density is reduced to ~50% by the introduction of porosity, whilst there is a large decrease in the permittivity [4]. This indicates that there is potential to improve the energy harvesting FOM by introducing porosity as a second phase into ferroelectric ceramics. In addition to the FOM it is also beneficial to consider the impact of the presence of porosity on the electromechanical coupling coefficients, which determine the efficiency of energy

conversion from mechanical to electrical energy, or vice versa. The longitudinal coupling coefficient is given by:

$$k_{33}^2 = d_{33}^2 / (\epsilon_{33}^T \cdot S_{33}^E) \quad (3)$$

where S_{33}^E is the mechanical compliance in the 3-direction when a force is applied along the same axis. As a result there is a complex balance between the variation of d_{33} , ϵ_{33}^T and S_{33}^E with porosity.

The electromechanical properties of a piezo-composite, such as a porous ferroelectric, are highly dependent on the structure, which is classified by a two-digit notation first described by Newnham et al. [5]. The first digit refers to the active (piezoelectric) phase and the second to the inactive phase. The number assigned to each phase depends on the dimensionality of the interconnectivity and can range from 0 (isolated particles) to 3 (full interconnection in all directions). A 3-3 piezo-composite therefore has a fully connected ceramic phase with fully open porosity distributed throughout. By changing the structure it is possible to tune the properties such as piezoelectric strain coefficients, permittivity and mechanical compliance, which in turn affect both the FOM (Eqn. 2) and electromechanical coupling coefficient (Eqn. 3).

In this work 3-3 barium titanate structures have been produced with a range of porosities so as to determine the potential benefits of porous materials for piezoelectric energy harvesting and the impact of porosity on the relevant figures of merit. Barium titanate has been chosen for this study because the processing is less complicated than that for PZT as the ceramics can be sintered in air.

Experimental

Barium titanate powder (*Ferro, UK*) was ball milled for 24 hours with zirconia media and distilled water. Dense and low porosity samples (3-20% open porosity) required the addition of a small amount of binder, polyethylene glycol (PEG) (*Sigma Aldrich, UK*), to the BaTiO₃ powder prior to the milling stage to enable crack-free pressing. After ball milling, the powder was dried over night before sieving through a 150µm mesh. A range of porosities (10-72vol%) was obtained via the burned out

polymer spheres (BURPS) method, whereby a volatile pore forming agent (PFA), PEG, was mixed with the sieved BaTiO₃ powder in varying proportions by weight. The PFA burned out during sintering to form ceramic structures with a high degree of open porosity. Dense samples were also produced with no additional PEG, other than that used as binder. The powder was uniaxially pressed at 300MPa to form pellets 13mm in diameter and weighing 0.7g. Pellets were sintered in air at 1300°C for two hours, including a two hour dwell stage at 400°C on the up-ramp to burn out the binder/PFA, with a ramp rate of $\pm 60^\circ\text{C/h}$. XRD analysis was performed on a dense sample and a high porosity sample to confirm that a fully perovskite structure had formed. Samples were ground flat and cleaned in ethanol prior to determining the density and apparent porosity using the Archimedes method. Silver electrode paint (*RS Components*) was applied to all samples prior to corona poling in air at 115°C with a 14kV field applied from a 35mm point source. This poling procedure was chosen over poling in oil due to envisaged difficulties cleaning porous samples post-poling, as oil was likely to penetrate the porous structures. Piezoelectric strain coefficient, d_{33} , was measured using a *Take Control Piezometer System PM25*, which applies an alternating force of $\pm 0.1\text{N}$ at a frequency of 97Hz and measures the electrical charge generated. The dielectric properties of the materials were measured using impedance spectroscopy (*Solartron 1260 and 1296 Dielectric Interface*) with an AC voltage of 100mV applied over a frequency range of 0.1Hz-1MHz and used to calculate the unclamped (constant stress) permittivity.

Results and Discussion

Comparing data obtained via the Archimedes method for relative density and apparent porosity indicates that the connectivity of all pellets was a mixture of 3-0 and 3-3 connectivity. This was determined by subtracting the sum of the apparent (open) porosity (3-3) and the relative density from 100% to give the closed porosity (3-0). For the porous ceramic manufactured with $\geq 15\text{wt\%}$ PFA there was significantly more open porosity than isolated porosity, as shown in Fig. 1 as a plot of PFA against the fraction of open porosity compared to the total porosity. Relatively good control over the final porosity/relative density was achieved using the BURPS process, although the process had to be

altered for samples with <12.5wt% PFA due to difficulties obtaining crack-free pellets. The grain size in dense and two porous samples, with 40% and 60% relative densities, was investigated using scanning electron microscopy (SEM) and no significant change was identified in the bulk ceramic, with grain width generally in the range of 10-30 μm . In the immediate vicinity of a pore the grain size was found to decrease in both dense and porous samples, where the pores are thought to act as pinning sites, inhibiting grain growth. Pores formed due to the burn off of the PFA were spherical in shape with diameters ranging between 100-400 μm . SEM images of samples with 95% and 40% relative density are shown in Fig. 2a and 2b, respectively.

The variation of d_{33} with porosity is shown in Fig. 3. As expected, the dense samples exhibited the highest piezoelectric strain coefficients, thought to be due to more complete poling of the samples. Reducing the relative density via the introduction of porosity is found to reduce the strain coefficient, although above ~40% the response remains relatively high at ~75% of the maximum d_{33} values achieved for dense BaTiO₃. This is a similar trend to that observed for porous PZT synthesised via the BURPS process [4, 6]. The large spread in data is attributed to difficulties in the poling procedure, which appears to be affected by ambient conditions, such as temperature and humidity, and controlling them in the experimental set up is not possible. The decrease in d_{33} in high porosity samples (<40% relative density) may be due to incomplete poling of the BaTiO₃ phase caused by lower breakdown strength that occurs in highly porous dielectric ceramics and complex electric field distribution resulting from a mixture of low and high permittivity phases. Pores are also likely to increase stress concentrations that lead to depolarisation of the material [6] and also limit the grain size in their immediate vicinity, which is thought to inhibit domain motion [7], therefore reducing the achievable level of spontaneous polarisation. Slightly lower d_{33} values than might be expected were observed in samples with a relative density in the range of 75-90% theoretical. In order to produce crack-free samples in this range a small amount of binder was added to the BaTiO₃ powder prior to ball milling, which may have affected the microstructure or bulk structure in a way that suppresses the piezoelectric response.

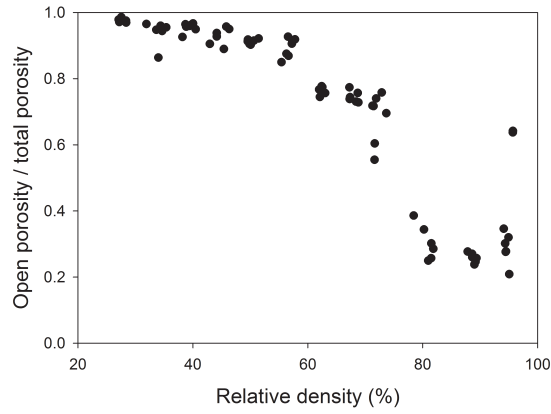


Fig. 1: Fraction of open porosity in BaTiO_3 compared to the total porosity plotted against relative density. Data obtained via the Archimedes method. The high values of the ‘open porosity/total porosity’ ratio at low relative density indicate that nearly all the porosity is open, i.e. pores are fully interconnected.

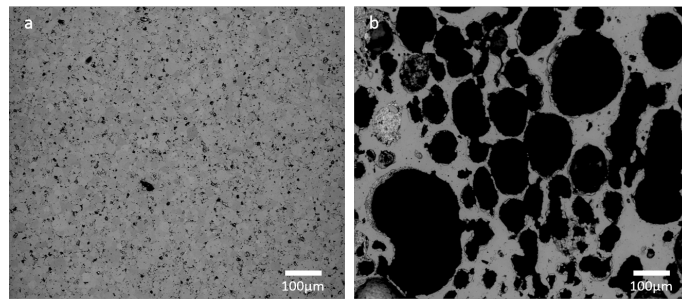


Fig. 2: a) Dense BaTiO_3 microstructure and b) Porous BaTiO_3 (~40% relative density) with spherical pores formed during burn off of the volatile additive, PEG.

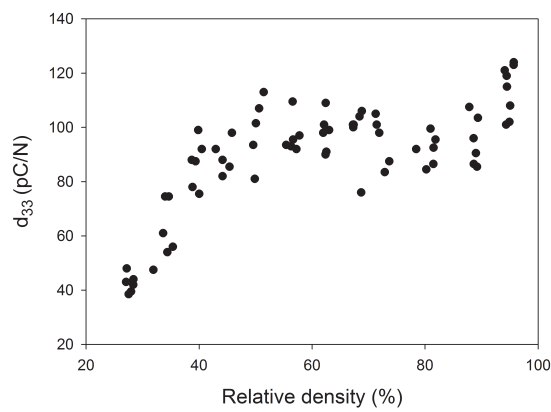


Fig. 3: Variation of piezoelectric strain coefficient, d_{33} , with relative density. Values remain relatively high (>100pC/N) up to high porosity levels (~40% relative density).

The permittivity of the porous ceramics was calculated from complex electrical impedance data measured across a range of frequencies and is reported here as the constant stress (unclamped) permittivity at 1kHz as a function of relative density (Fig. 4). The permittivity was found to significantly decrease with the introduction of porosity, as the volume fraction of high permittivity BaTiO₃ was reduced. This is in agreement with previous studies [4-6] and is one of the key reasons for investigating the effect of porosity on piezoelectric energy harvesters.

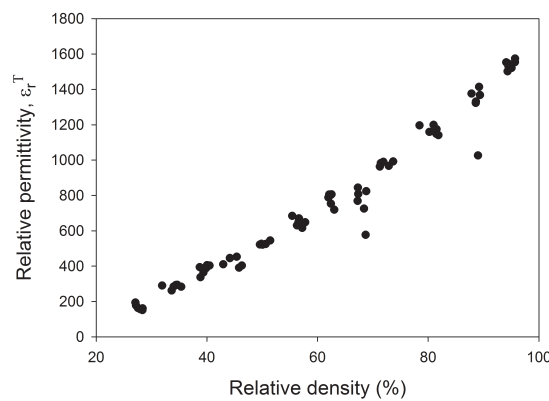


Fig. 4: Variation in relative permittivity (ϵ_{33}^T) with relative density. As porosity is increased (relative density decreased) permittivity decreases.

Fig. 5 shows the variation of piezoelectric energy harvesting FOM₃₃, calculated using Eqn. 2, against relative density. Low permittivities in high porosity samples, coupled with relatively high d_{33} values above 40% relative density, result in a broad peak in the FOM₃₃ from 40-50% relative density. This is a similar phenomenon to that observed in porous PZT for hydrophone applications where $d_h \cdot g_h$ reaches a maximum at a similar porosity [4]. Compared with dense BaTiO₃, a three-fold increase in the harvest FOM₃₃ is observed in these samples. At high porosities (<40% relative density), there is a fall in FOM₃₃ despite very low permittivities measured in these samples; this is a result of the low d_{33} values of these highly porous materials.

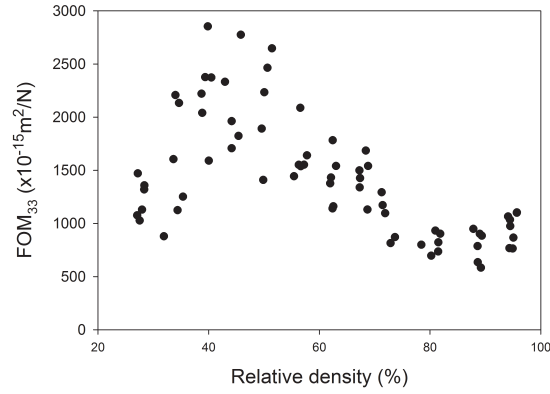


Fig. 5: Energy harvesting figure of merit (FOM_{33}) calculated across full range of relative densities, using Eqn. 1. A broad peak is observed between 40 and 50% due to significant reductions in permittivity at this point but only relatively small reduction in d_{33} .

Conclusions

Porous BaTiO₃ has been synthesised using the BURPS process, with polyethylene glycol used as a volatile pore-forming species, and their potential for energy harvesting evaluated compared to conventional dense BaTiO₃. The relative density and open and closed porosity were characterised and microstructural analysis demonstrated that the porous composite structures changed from a 3-0 configuration (isolated pores) to a 3-3 configuration (interconnected pores) as the level of porosity was increased. The porous materials were characterised in terms of their piezoelectric and dielectric properties, which were then used to calculate a piezoelectric energy harvesting FOM_{33} for low frequency, off-resonance mechanical excitation. A maximum FOM_{33} of 2.85 pm²/N was achieved at a relative density of ~40% (~60% porosity), a near three-fold increase compared with the dense samples. This significant improvement in the FOM_{33} was the result of a large reduction in permittivity at this porosity level along with a relatively small reduction in d_{33} . The implication of this work is that for a given applied stress the energy generated within a material with an appropriate pore volume fraction can be significantly larger than its dense counterpart. Further investigation is required to determine the direct mode electromechanical coupling coefficient, k_{33}^2 , of BaTiO₃ at different

relative densities, which would show the effect of porosity on the efficiency of conversion from mechanical to electrical energy.

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